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Study on optical and electrical switching properties and phase transition mechanism of Mo^{6+}-doped vanadium dioxide thin films

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In the present work using V_2O_5 and MoO_3 powders as precursors, a novel method, the inorganic sol-gel method, was developed to synthesize Mo^{6+} doped vanadium dioxide (VO_2) thin films. The structure, valence state, phase transition temperature, magnitude of resistivity change and change in optical transmittance below and above the phase transition of these films are determined by XRD, XPS, four-point probe equipment and spectrophotometer. The results showed that the main chemical composition of the films was VO_2, the structure of MoO_3 in the films didn't change, and the phase transition temperature of the VO_2 was obviously lowered with increasing MoO_3 doped concentration. The magnitude of resistivity change and change in optical transmittance below and above phase transition were also decreased, of which the magnitude of resistivity change was more distinct. However, when the MoO_3 concentration was 5 wt%, the magnitude of resistivity change of doped thin films still reached more than 2 orders, and the change in optical transmittance below and above phase transition was maintained. Analysis showed that the VO_2 doped films formed local energy level, and then reduced the forbidden band gap of VO_2 as the donor defect changing its optical and electrical properties and lowering the phase transition temperature. © *2004 Kluwer Academic Publishers*

1. Introduction

Vanadium dioxide (VO_2) has attracted much interest because it was found to undergo a phase transition from a metal to a semiconductor when the temperature decreases to approximately 68°C. This transition corresponds to a first-order displacive distortion from a tetragonal metallic phase into a monoclinic semiconducting phase, and exhibits dramatic changes in electrical, optical and magnetic properties [1–4]. Thermal expansion causes damage to bulk VO_2 during repeated cycling through the transition, but VO_2 thin films are more tolerant to repeated heating and cooling [2]. Since the first report on its phase transition in 1959 [5], VO_2 thin films have been extensively studied and a wide variety of applications have been proposed, e.g., temperature sensing devices [6], optical switching devices [7, 8], modulator and polarizer of submillimetre wave [9], optical data storage medium [10], variable reflectance mirrors [2], and energy-conserving coatings for windows [1].

However, it is required in most cases that the phase transition temperature of VO_2 thin films be reduced to near the ambient, so great efforts have been made in order to lower the phase transition temperature for practical application. It has been shown previously that the phase transition temperature of VO_2 thin films can be modified by doping [8, 11–18]. It is lowered with high-valent cations (Nb^{5+}, Mo^{6+}, Ta^{5+}, W^{6+}) that generate a donor-like defect, whereas it is increased with low-valent cations (Al^{3+}, Cr^{3+}, Fe^{3+}) that generate an acceptor-like defect. Doping of VO_2 thin films by sputtering [13, 19], high-energy ion implantation [20], introducing dopants to the precursors [21] and sol-gel methods [12, 22] has been previously reported. Due to the advantages of high purity, homogeneity, stoichiometry, and the ease of doping, the sol-gel processing has become one of the best approaches to prepare doped VO_2 films on silica glass substrates [16, 23]. The sol-gel route often uses expensive and usually unstable vanadium alkoxides as precursors, so to avoid

this disadvantage, we have developed a new preparation method to synthesize doped VO_2 thin films based on a quenching method. It is called the inorganic sol-gel method, because the former uses vanadium alkoxides as precursors whereas the latter uses V_2O_5 and MoO_3 powders as precursors [2, 6].

In this paper, we studied Mo^{6+} doped VO_2 thin films prepared by the inorganic sol-gel method, and analyzed the effect of Mo^{6+} on electrical and optical switching properties of VO_2 thin films and phase transition mechanism.

2. Experimental

The thin films doped with MoO_3 had been prepared by using the highly pure (99.9%) V_2O_5 and MoO_3 powders. The chemical composition of precursors was $(100 - x)V_2O_5 - x\,MoO_3$ (where $x = 1.0, 2.0, 3.0, 4.0$, and 5.0 wt%). The combined constituent chemicals were melted in a ceramic crucible at 800–900°C for 20–30 min in an ambient atmosphere, then poured into distilled water at room temperature. A brownish sol of V_2O_5 and MoO_3 was formed with the water. Silica glasses were used as substrates (10 × 20 mm, 2 mm thick). The substrates were spin-coated with doped V_2O_5 sol then dried at room temperature for 2 days to obtain Mo ion doped V_2O_5 gel films. Thicker films could be obtained by repeating this process. The Mo ions doped V_2O_5 films were heated in a vacuum furnace at 500 ± 10°C for 10 h. The heating rate was 3–4°C/min. The vaccum chamber was fed with low-pressure air, operating at 1–5 Pa.

The film thickness was measured with a 6JA interference microscope. The structure of the samples was determined by XRD using a P/max-3C (Japan) diffractometer and Cu K_α radiation. The valence state of vanadium was studied by XPS using a Escalab 220-IXL spectrometer. The spectral transmittance in the wavelength range 300–2500 nm at normal incidence was obtained with the Perkin-Elmer Lambda 9 spectrophotometer; the measurement was performed with the samples kept at constant temperatures of 20 and 50°C, corresponding to the semiconductor and metal states, respectively. The electrical resistance of the films was measured as a function of temperature using a four-point probe management associated with a Hewlett Packard HP 3456A multimeter, and a Peltier device coupled with an automated temperature control (rate 2°C/min).

3. Results and discussion

3.1. X-ray diffraction analyses

Fig. 1 shows XRD patterns of the sample containing 3 wt% of MoO_3. The film thickness is approx 600 nm. Strong peaks of monoclinic VO_2 are observed and a few peaks of V_2O_5 are also observed, referenced with standard pattern (identified on the basis of ASTM data, Card No.9-142 and 9-387) of the X-ray diffraction system. No other vanadium oxides are detected. In addition, MoO_3 peak is not observed in the XRD pattern. The reason is that MoO_3 in doped thin films as the solute donor forms solid solutions with VO_2.

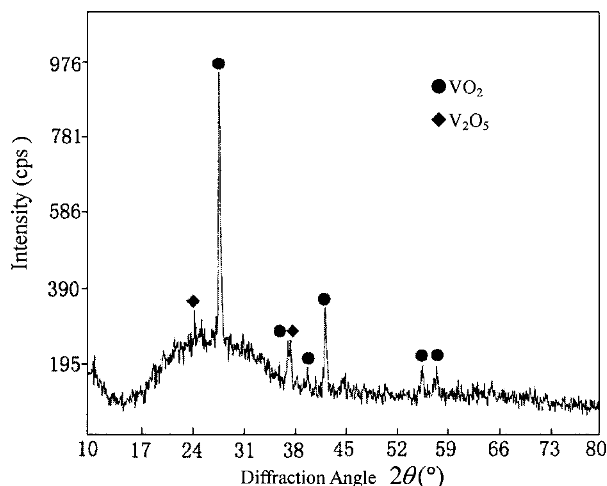


Figure 1 X-ray diffraction pattern of the sample containing 3 wt% of MoO_3.

3.2. X-ray photoelectron spectroscopy (XPS) analyses

The raw surface XPS spectra of the sample containing MoO_3 (3 wt% of MoO_3) are shown in Figs 2 and 3. Fig. 2 shows that peak $V2p_{3/2}$ of the same sample can be separated into V^{4+} peak and V^{5+} peak at binding energies 516.18 and 517.85 eV, respectively. The area

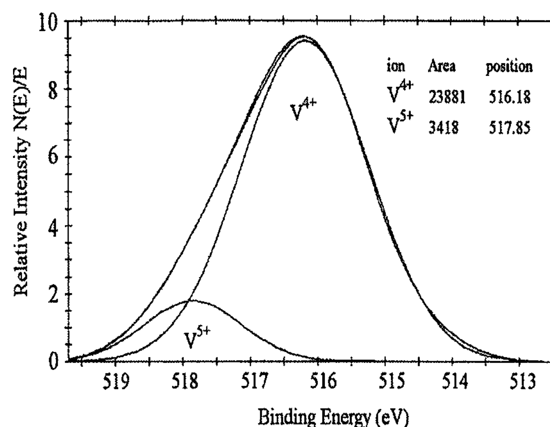


Figure 2 Separated $V2p_{3/2}$ peaks of the sample containing 3 wt% of MoO_3 ($V2p_{3/2}$ peak of the sample at binding energy 517.1 eV, $V2p_{3/2}$ peak of V(IV) at binding energy 516.18 eV, $V2p_{3/2}$ peak of V(V) at binding energy 517.85 eV).

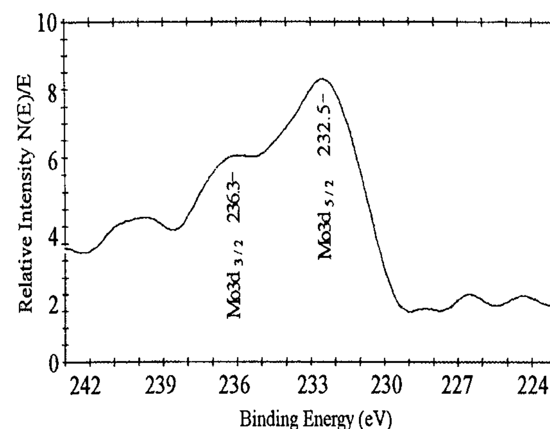


Figure 3 Mo3d peaks of the sample containing MoO_3 ($x = 3$ wt%).

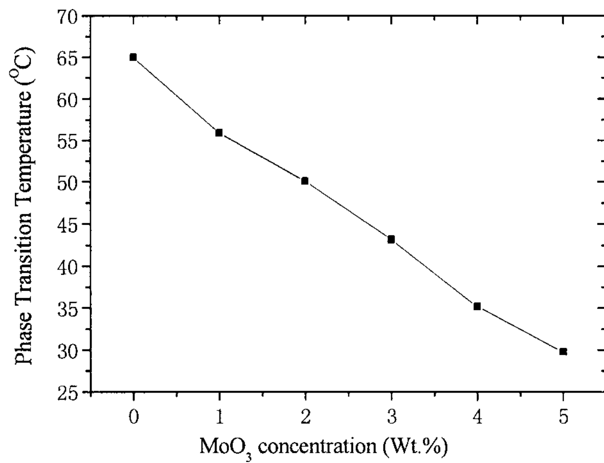


Figure 4 The effect of MoO_3 doped concentration on the phase transition temperature of the samples.

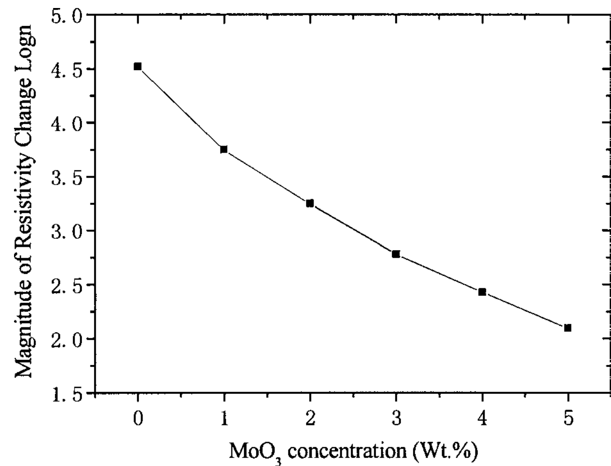


Figure 5 The effect of MoO_3 doped concentration on the magnitude of resistivity change of the sample (Log n, $n = \rho$ (below phase transition)/ρ (above phase transition)).

under the curve represents the ratio of V ions in the different valences V^{4+} and V^{5+}, leading to the conclusion that the proportion of V^{4+} in the sample is 87.55%. Fig. 3 shows the Mo3d peaks of the samples. According to the standard binding energy of MoO_3, it is shown that there is a little MoO_3 in the sample, and the existent form of Mo ions in these VO_2 films is Mo^{6+}.

3.3. The phase transition temperature of doped thin films

The phase transition temperature was determined from resistivity measurements. The phase transition temperature is related by

$$T_c = (T_1 + T_2)/2 \qquad (1)$$

where T_c is the phase transition temperature, T_1 and T_2 are temperature of electrical resistance dramatic change of the films in heating and cooling process, respectively. The effect of MoO_3 dopant concentration on the phase transition temperature of the VO_2 is shown in Fig. 4. From Fig. 4 it can be observed that the phase transition temperature is lowered with increasing MoO_3 concentration. When the MoO_3 concentration is 5 wt%, the phase transition temperature of the VO_2 films is lowered to about 30°C.

3.4. Electrical switching properties of doped thin films

The effect of MoO_3 concentration on the magnitude of resistivity change of the samples is shown in Fig. 5. With increasing MoO_3 concentration, it is shown that the magnitude of resistivity change is also reduced. However, for MoO_3 dopant concentration of less than 5 wt%, the magnitude of resistivity change of VO_2 films is still more than 2 orders, and the electrical switching properties of VO_2 thin films can still be maintained.

3.5. Optical switching properties of doped thin films

It is possible to evaluate the optical transmittance over near IR for doped VO_2 thin films on silica glass sub-

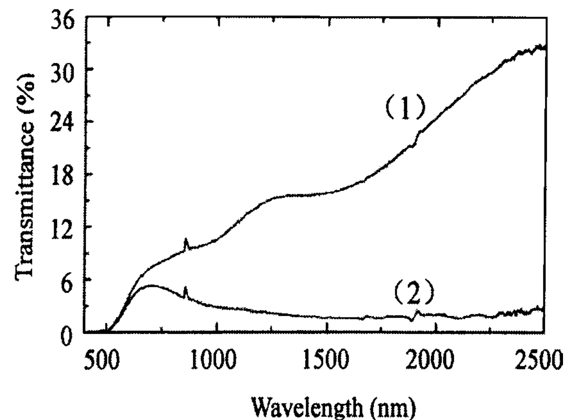


Figure 6 Transmission spectra for the Mo^{6+} doped thin films below and above phase transition (3 wt% of MoO_3): (1) 20°C and (2) 50°C.

strates. Fig. 6 shows spectral transmittance at 20 and 50°C, corresponding respectively to the semiconductor and metallic states for the sample containing MoO_3 (3 wt% of MoO_3). The film thickness is approx 600 nm, and spectrophotometry analysis is performed in the 300 nm $\leq \lambda \leq$ 2500 nm wavelength range. For transmittance measurement made below the phase transition temperature, there is a monotonic increase in the transmittance with wavelength, which reaches about 33% at 2500 nm. Above the phase transition temperature, there is an increase in the transmittance up to a peak value of about 5% at 700 nm, and thereafter it decreases to about 3% at 2500 nm. From Fig. 6 it can be calculated that the change in optical transmittance at 2500 nm between the two states reaches approx 30%. The change in optical transmittance of doped thin films below and above phase transition temperature is less than that of undoped VO_2 thin films [3, 4, 10], it is still substantial. As a consequence, the practical application of optical switching properties of doped VO_2 thin films is viable. In addition, from Fig. 6 it is observed that the change in optical transmittance of doped VO_2 thin films (3 wt% of MoO_3) takes place below 50°C, showing the transition temperature of the film has indeed been lowered.

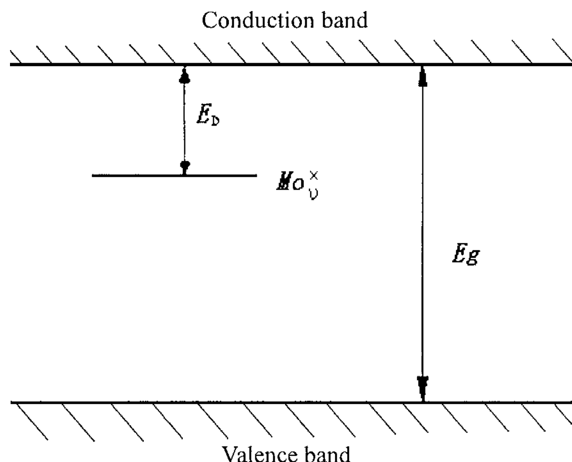
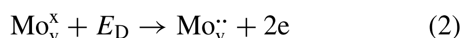


Figure 7 The diagram of local energy level formed in the VO_2 thin films by doping with MoO_3.

3.6. Discussion

From the XPS analysis it is known that the structure of MoO_3 in VO_2 thin films does not change and the existent form of Mo ions in VO_2 thin films is Mo^{6+}. The partial replacement of V^{4+} by Mo^{6+} results in doped thin films with composition $V_{1-x}MO_xO_2$. When VO_2 thin films are doped with Mo^{6+}, the impurity defect $Mo_V^{\cdot\cdot}$ is formed in crystal configuration of the VO_2 film. The impurity defect $Mo_V^{\cdot\cdot}$ is equivalent to a bivalent positive ion relaxedly bound with two electrons, namely $Mo_V^{\cdot\cdot} + 2e$, and its effective charge sign was denoted as Mo_V^x. The ionization of electrons from Mo_V^x is given by [23]



$$Mo_V^x + E_D \rightarrow Mo_V^{\cdot\cdot} + 2e \tag{2}$$

Doping of VO_2 with Mo^{6+} is equivalent to the donor defect Mo_V^x. The negative charge ionized from the donor defect Mo_V^x is situated on the local energy level formed in forbidden band and located at the bottom of the conduction band, which reduces the forbidden band gap. The local energy level formed in the forbidden band of VO_2 by doping with MoO_3 is shown in Fig. 7. The electrical switching properties of VO_2 thin films are modified as a result of redundant negative charge of the donor defect Mo_V^x, which can be excited and transitted to conduction band at a lower temperature, making the phase transition temperature lower. Different concentrations of Mo^{6+} in the VO_2 thin films will induce different amounts of donor defects Mo_V^x, and the phase transition temperature is lowered with increasing MoO_3 doped concentration. However, the electrical switching properties of VO_2 thin films are primarily determined by the crystal configuration of VO_2. Although MoO_3 in doped VO_2 thin films changes the energy level configuration of VO_2, the change of VO_2 crystal configuration, namely the donor defect Mo_V^x formed in VO_2 crystal configuration, has an adverse effect on the process of electron transition. It is evident that the resistance of electron transition is augmented, which is the reason that the magnitude of resistivity change is reduced with increasing MoO_3 concentration.

Below the phase transition temperature (as a result of VO_2 forbidden band) VO_2 thin films exhibit optical transmittance to photons, especially photons in IR wave band with lower energy, whose optical transmittance is higher. When VO_2 is doped with MoO_3, a local energy level is formed, which reduces the forbidden band gap of VO_2. Electrons in local energy level are more readily excitated and transitted to conduction band than that of undoped VO_2 thin films producing free electrons. These free electrons can absorb photons of different wavelengths (energies), consequently, the optical transmittance of doped VO_2 thin films is less than that of undoped VO_2 thin films below phase transition temperature. Above the phase transition temperature, both doped VO_2 films and undoped VO_2 films are metallic, current carrier are nearly unrestricted, and the forbidden band nearly disappears, so all photons of different frequencies are almost adsorbed. These electrons adsorbing photon energy are excitated and relax, energy being released as light and heat. This process occurs readily and largely blocks photon transmission. As a result, optical transmittance of both doped VO_2 thin films and undoped VO_2 thin films is rather low in the metallic state. Consequently, the change in optical transmittance of doped VO_2 thin films below and above the phase transition is lower than that of undoped VO_2 thin films. In addition, different concentrations of Mo^{6+} in the VO_2 thin films will form different amounts of the donor defects Mo_V^x, hence it can be concluded that the substantial change in optical transmittance of doped VO_2 thin films below and above the phase transition is lowered with increasing MoO_3 concentration.

4. Conclusions

Using V_2O_5 and MoO_3 powders as precursors, high quality Mo^{6+} doped VO_2 thin films are prepared by the inorganic sol-gel method. The composition of the doped thin films was primarily VO_2, the structure of the MoO_3 in VO_2 thin films didn't change according to XPS. The phase transition temperature of the doped thin films was lowered with increasing MoO_3 dopant concentration, but the magnitude of resistivity change and change in optical transmittance between the two states were also lessened, of which the magnitude of resistivity change was more distinct. However, for MoO_3 concentration of not more than 5 wt%, the magnitude of resistivity change of the doped thin films still reached more than 2 orders, and the substantial change in the optical transmittance below and above the phase transition was retained. The doped VO_2 films are therefore still acceptable for practical applications requiring optical/electrical switching properties of VO_2 thin films.

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